Towards Understanding the pH sensitivity of few layer graphene

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Introduction

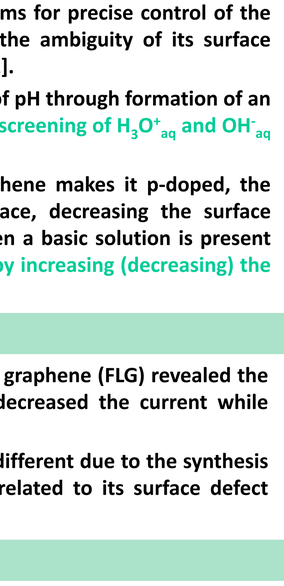
- pH, the negative logarithm of [H_3O^+], is a vital element of many chemical reactions, particularly in water quality determination. The solubility, complex formation of chemical species, redox reactions, and efficiency of disinfectant chemistry all depend on the pH of the solution [1].
- Graphene-based pH sensors have shown to be promising platforms for precise control of the pH; however, the hydrophobic nature of graphene as well as the ambiguity of its surface chemistry have limited its extensive applications as a pH sensor [2].
- A monolayer defect-free Graphene often perceives the variation of pH through formation of an electrical double layer (EDL) on the surface and capacitive charge screening of $H_3O^+_{aq}$ and OH^-_{aq} to the surface [3].
- Since the presence of oxygen based functional groups on graphene makes it p-doped, the acidic solution screens negative charge to the graphene surface, decreasing the surface conductance. In contrast, the surface conductivity increases when a basic solution is present [4]. Therefore, it is expected to increases (decrease) the current by increasing (decreasing) the pH.

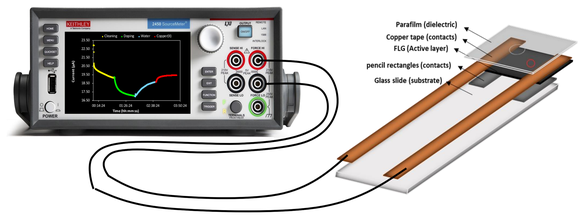
Research Motivation

- The chemiresistive pH sensor made by liquid exfoliated few-layer graphene (FLG) revealed the opposite behavior of monolayer graphene; increasing the pH decreased the current while decreasing the pH increased the surface conductivity.
- Since the defectivity levels of these two graphene structures are different due to the synthesis process, the origin of the pH sensitivity of graphene must be related to its surface defect density. But. The question is how?

Experimental section

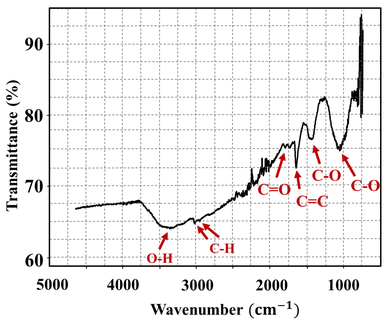
- We have developed a chemiresistive sensor that uses a FLG film as the transducing element. The fabrication steps of the sensor are shown in the flow chart on the right side The sensing event modifies its electron transport properties, which leads to a change in resistance. By probing the sensor with a small voltage, these changes can be monitored (shown in below Figure).
- Sonication intensifies solvent-FLG interactions through fabrication process. Therefore, the prepared FLG is defective.



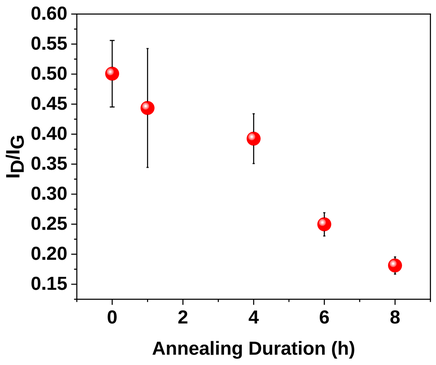


Defects in Few-layer Graphene

- By sonication of FLG and chemical interaction of solvent (IPA/H_2O), oxygen based functional groups are generated on graphene surface (as seen in FTIR spectra on the right side). These groups include carbonyl, carboxyl, ketone, ethers, hydroxyl [5].
- To obtain a range of defectivity on FLG, samples were annealed under N_2/H_2 environment. The presence of H_2 at high temperatures (500 °C) reduces the surface functional groups [6]. Therefore, by controlling the annealing duration, a wide range of defective FLG was obtained.

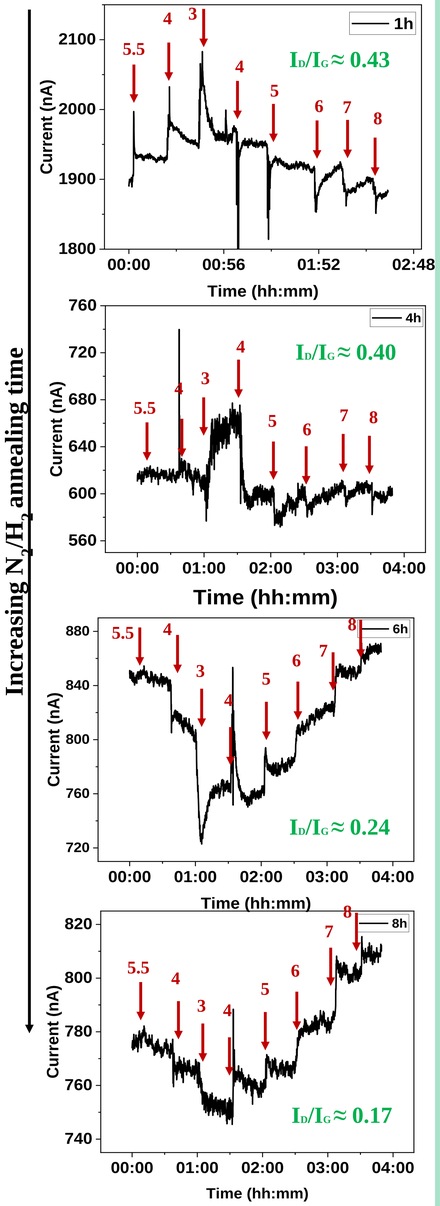


- The annealed samples were characterized by Raman spectroscopy and the ratio of D band (related to defects) to G band (for sp^2) hybridization of graphene was plotted (shown in Figure on the right side).
- The ratio of I_D/I_G indicates how defective is the FLG [7]. As seen, increasing the annealing duration decreases the I_D/I_G considerably, from 0.5 to 0.17.
- This demonstrates the surface reduction of FLG by thermal annealing in the presence of H_2 (g).



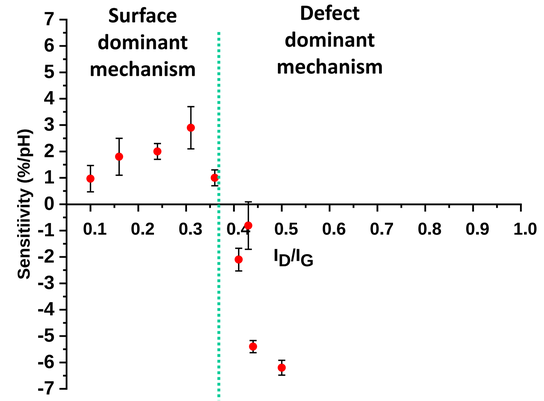
pH sensing data

- By exposing the annealed samples, it is seen that 1h annealed shows the opposite behavior in pH and current, giving a calibration curve with a negative sign (as seen for as prepared FLG). This is exactly the opposite of defect-free graphene.
- By increasing the annealing duration to 4 h (second figure), the sensor only responds to pH 3 and 4 and is almost insensitive at high pH. At this duration, the weakly bonded groups such as –OH are reduced and groups like –COOH are still on the surface. Upon protonation of $–COO^-$ to –COOH, the surface is p-doped and therefore, current increases. This justifies the jump in current at pH 3- 4 since the pK_a of COOH groups is estimated to be 3.79 [8].
- By 6h annealing, the pH sensing behavior is now reversed; an increase in pH increases the current and vice versa. This resembles the behavior of defect-free graphene, offering a positive slope in calibration curves (pH sensitivity). Still, the jump in current at pH 4 could be associated to presence of –COOH.
- By 8h annealing, the stepwise behavior becomes clear with lower noises. This area is where the surface EDL interactions are dominant and control the pathways by which, graphene perceives pH variation.



Conclusion

- The overall relationship between the pH response of FLG and its defectivity (represented by the I_D/I_G ratio) is illustrated below, accounting for both mechanisms. The left and right regions of the graph represent dominance of the surface induced response and dominance of the defect response, respectively. In the right region, increasing the defect density initially leads to a higher sensitivity (negative values, i.e., the negative slope of the calibration curve) until it saturates at a specific defect density. After this point introducing more defects will not considerably affect the sensitivity. By surface reduction to I_D/I_G around the crossover point (here it is at I_D/I_G = 0.35), the curve enters the region of low defectivity at the left of the graph, where the double layer induced mechanism dominates. By continuing to reduce the I_D/I_G ratio, the slope of the calibration curves will become more positive. However, since a defect-free (or at least very low defect) graphene surface is hydrophobic, the sensitivity will start to drop significantly as we approach zero. At this point, graphene repels the water completely and no interactions can occur



Acknowledgments

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CCEM Canadian Centre for Electron Microscopy

Adronove research group

Selvaganapathy research group

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